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THE HABIT OF ASBESTIFORM AMPHIBOLES: IMPLICATIONS FOR THE ANALYSIS OF BULK SAMPLES

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ABSTRACT: Evidence on the carcinogenicity of fibrous minerals supports the conclusion that amphiboles must form in an asbestiform habit in order to pose a risk to human health. Furthermore, the asbestiform habit controls many of the physical properties of asbestos. Because of the distinctive characteristics of the asbestiform habit, populations of asbestiform amphiboles can be distinguished from populations of amphibole cleavage fragments by light microscopy. Populations of asbestos fibers longer than 5 μm are characterized by fibers that occur in bundles, are often curved, and have very high aspect ratios (mean aspect ratio > 20:1 - 100:1) and narrow widths, usually less than 0.5 μm. It is inappropriate to apply a 3:1 aspect ratio criterion to identify amphibole asbestos. Other minerals that crystallize in a habit similar to asbestos do not necessarily pose the same risk because factors such as friability, biodurability, bioavailability and surface chemistry are important in determining carcinogenicity of mineral fibers.

KEY WORDS: asbestos, asbestiform, amphibole, mineralogical characteristics

Introduction

When the Occupational Safety and Health Administration (OSHA) issued the first permanent standard for exposure to asbestos dust in 1972 [*1*], the names of three minerals,

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tremolite, actinolite, and anthophyllite, were included without the specification that they must be asbestiform. In 1992, the Occupational Safety and Health Administration revised its asbestos regulations so that only the asbestiform varieties of these minerals were covered. [2] During the 20 years separating these rulings, research was conducted that addressed the following issues: 1) what are the properties of amphibole-asbestos, 2) which of these properties make them carcinogens, 3) what is the carcinogenic potential of amphiboles that are not asbestiform, and 4) how can asbestiform amphiboles be differentiated from other amphibole habits. In this paper, I will summarize the mineralogical characteristics of asbestiform amphiboles with particular emphasis on differentiating among the habits of amphibole in the analysis of bulk samples.

The Mineralogical Properties of Amphibole Asbestos

A mineral name specifies two things about the naturally occurring crystalline solid it identifies: the relative proportions of the major elements that make it up and the arrangement, or structure, of the atoms. Associated with the chemical composition and atomic structure are physical properties by which the mineral can be identified. These include specific gravity (or density), indices of refraction and other optical properties, hardness, color, luster, cleavage, streak, solubility, electrical conductivity, and so forth.

Sometimes a mineral may form with a habit of growth or an unusual color that distinguishes it from the more common occurrences, and a varietal name is used to designate this form. Well known examples can be found in minerals that are prized as gems where color and clarity are the properties that determine the variety. For example, emerald and aquamarine are varieties of the mineral beryl, and ruby and sapphire are varieties of the mineral corundum. Because varietal names are usually assigned specifically on the basis of external appearance, varieties can not be distinguished from other habits of the same mineral by bulk techniques of analysis such as x-ray diffraction. Furthermore, if the appearance of a mineral specimen is severely altered by grinding to a fine powder, it is usually impossible to assign a varietal name, and it may be appropriate to conclude that it is no longer a particular variety at all. For example, an emerald crushed to a fine power can not be distinguished from a powdered aquamarine, although both powders remain easily identifiable as the mineral beryl. In the same way, because asbestos is a varietal name, if asbestos is reduced to a powder such that its distinguishing physical properties are destroyed, it is no longer asbestos.

The amphiboles regulated in their asbestiform variety

are usually listed as amosite, crocidolite, tremolite-asbestos, actinolite-asbestos, and anthophyllite-asbestos. These are the asbestiform varieties of the minerals grunerite, riebeckite, tremolite, actinolite, and anthophyllite, respectively. (Amphibole nomenclature is detailed in [3].) Amphiboles may be found in nature in compact masses; in stubby or acicular prismatic crystals, either singly or intergrown; in fine, brittle needles which, when separated by open space, are referred to as byssolite [4]; or as long, strong, flexible, fibers, which are usually composed of very thin single crystals called fibrils, and which are capable of being woven, a habit that is referred to as asbestos. Amphiboles may be 'fibrous', i.e., they give the appearance of being composed of fibers, whether or not they are actually made up of individually separable fibers. While all asbestiform amphiboles are fibrous, not all fibrous amphiboles are asbestiform.

In modern usage, only grunerite-asbestos and riebeckite-asbestos go by varietal names, amosite and crocidolite respectively. While crocidolite is generally recognized by mineralogists as a varietal name for riebeckite-asbestos, (although technically discarded in the official amphibole terminology [3]) the term 'amosite' is not, because it is a commercial term for a mineral product (Asbestos Mines of South Africa). However, AMOSite is composed mainly of the mineral grunerite in its asbestiform habit, and amosite remains the varietal name for grunerite-asbestos for regulatory purposes, despite attempts by mineralogists to discredit it. Tremolite, actinolite, and anthophyllite are mineral names and as such do not specify a particular habit or mineral variety. To specify the asbestiform variety, tremolite-asbestos, actinolite-asbestos and anthophyllite-asbestos must be designated. For the latter three, the term 'asbestos' was omitted in OSHA regulations prior to 1992, (although it has always been used by EPA), and unfortunately today it is still occasionally disregarded.

The varieties of amphibole known as asbestos possess a set of physical properties that make them commercially valuable, properties which have been described extensively in the literature [5-11]. For thousands of years asbestos has been prized for the fact that it can be woven into a cloth that will not burn. Necessary for this application are long, thin, flexible silicate fibers that possess high tensile strength. In amphibole-asbestos, the flexibility and tensile strength are directly relatable to the dimensional properties and the conditions of growth. Tensile strength may be ten times greater than the massive varieties [12]. Walker and Zoltai [12] attribute the high tensile strength of asbestos to both the very small widths of fibrils and the small number of flaws on fibrillar surfaces. However, heating asbestos fibers to temperatures too low to produce structural modifications lowers their tensile

strength, suggesting that hydrogen bonds between fibrils, which are broken as water is lost during heating, may also contribute to tensile strength [*11*]. Further, it has been suggested that planar defects parallel to the fiber axis enhance tensile strength by mitigating the propagation of cracks and by providing sites of interplanar slip [*13,14*]. The flexibility of asbestos can be explained by both the small width and extreme aspect ratios of fibrils and by the fact that fibrils in bundles may slip past one another. The observation that anthophyllite-asbestos from the Paakila district in Finland has much lower flexibility and larger fibrillar widths than crocidolite from both the Cape Province in South Africa and the Hammersely Range in Western Australia is consistent with the conclusion that flexibility is inversely proportional to fibril width. Although amphibole-asbestos is cited for its chemical and electrical resistance, it has not been demonstrated that these properties are different from the nonasbestiform varieties.

Amphibole-asbestos fibrils range in width from about 1 to 0.01 μm. In some deposits the range in width is small; in others, it is large and may vary from one part of the deposit to another. Individual fibrils and bundles of fibrils may attain lengths of hundreds to thousands of times their widths. The geologic conditions that favor crystallization in the asbestiform habit include a water-rich fluid, probably at geologically low temperature, that is saturated or supersaturated with respect to the amphibole mineral. These conditions result in rapid nucleation at multiple sites and growth confined almost exclusively to one crystallographic direction (c-axis) usually without preferred orientation in the other two crystallographic directions [*15-18*]. The presence of some simple or complex ion (or ions) dissolved in this fluid may inhibit growth perpendicular to the fiber axis, effectively forming a barrier so that adjoining fibers remain separated. Thus, in asbestos, the individual fibrils are separate crystals, and they can be easily separated with hand pressure; their surfaces are surfaces of growth rather than breakage; and they are extremely thin and therefore can easily become airborne and be inhaled.

In most commercial deposits of amphibole-asbestos, the long axis of the fibrils are parallel to each other and perpendicular to the wall of the veins in which they are found. These are referred to as cross-fiber deposits. However, asbestos is also found in bundles that are parallel to the vein walls; the bundles may be interwoven, or they may occur in aggregates radiating out from an apex with shorter fibrils and fiber bundles filling in the spaces. Sometimes, asbestos occurs in mass fiber deposits in which the fibrils and fiber bundles occur without a predominant orientation. The Calidria chrysotile-asbestos deposit is such a mass fiber deposit. Mass fiber occurrences of amphibole sometimes result in a tough, compact rock from

which the fibers cannot be separated; these samples are not asbestos. The best example of this is the variety of actinolite known as jade.

Fibrillar surfaces are growth surfaces. In amphibole asbestos, they are faces in the [001] zone and are most commonly {100}, {110} ({210} for the orthorhombic anthophyllite-asbestos), and {010} [*15-17*]. For most samples of amphibole-asbestos, {100} is prominently developed, resulting in flat ribbon-like fibrils [*19,20*]. The ribbon-shape was confirmed for amosite and crocidolite by experiments with TEM and SEM that directly measured both width and thickness [*21*]. It is not uncommon to find sheet silicates such as talc, chlorite, and serpentine forming thin epitaxial layers on the outside of fibrils and occasionally in the spaces between them [*16,17*].

Rapid growth from supersaturated, low temperature, water-rich fluids in which there may be fluctuations in temperature, pressure, pH and concentration of dissolved ions, are the conditions that favor the development of defects in the structure of minerals. Three types of defects are common in amphibole asbestos: Wadsley defects parallel to (010) resulting from chain width errors, twinning on (100), and stacking faults parallel to (100) [*7, 22,23*]. Structural defects produce planes of weakness called parting (as opposed to cleavage which is weakness inherent in a "perfect" structure), and some separation of fibrils during comminution may actually be parting along these defect surfaces. However, (100) twinning, stacking faults, and Wadsley defects are not confined to the asbestiform habit of amphiboles; they may be well developed in some nonasbestiform amphibole specimens although they do tend to enhance elongation [*19,24*]. For example, byssolite fibers of tremolite and actinolite often exhibit optical properties and/or physical shapes that are consistent with extensive twinning on {100} [Verkouteren and Wylie, in preparation,*18*].

The fibrillar structure of the asbestiform habit results in anomalous optical properties [*18*]. With the exception of anthophyllite, asbestiform amphiboles are monoclinic. However, in cross-polarized light, asbestos fibers generally display parallel extinction, instead of the expected inclined extinction. Crocidolite and amosite were once thought to be orthorhombic like anthophyllite because of this property. In tremolite-asbestos and actinolite-asbestos, oblique extinction can sometimes be seen in the larger fibers that are not bundles. However, oblique extinction is not observed in crocidolite or amosite.

The Carcinogenicity of Amphibole Asbestos and the Asbestiform Habit

Although this paper is not intended to review the vast literature on the carcinogenicity of asbestos, it may be helpful to the reader to review some of the major studies that have address the role of fiber size. The most influential work was the animal experiments of Merle Stanton and co-workers published in 1981 [25]. From this work emerged the "Stanton Hypothesis": the carcinogenicity of inorganic particulate depends on dimension and durability rather than on physicochemical properties. It has been extended to include the following *corollaries*: the fibers of narrow width are the most carcinogenic, and carcinogenicity is proportional to the number of long, thin fibers in a material. Stanton et al. found that populations with abundant fibers longer than 8 μm and narrower than 0.25 μm were most closely linked to pleural tumor response in rats and that this response was independent of fiber type. The human experience with asbestos appears to support the conclusion that narrow widths contribute significantly to the carcinogenic potential of asbestos. Crocidolite from both the Cape Province of South Africa and from Western Australia has a the mean fiber diameter of less than 0.1 μm. Mesothelioma may account for as much as 18% of the proportional mortality for crocidolite workers [26]. In contrast, in the Transvaal, where both crocidolite and amosite with mean diameters of 0.21 and 0.24 μm respectively are mined, mesotheliomas are rare [27,28]. In Paakila, Finland, where the mean diameter is about 0.6 μm and widths less than 0.1 μm are quite rare [29], the mortality from mesothelioma among miners is less than 1% [30]. However, anthophyllite-asbestos is almost always intergrown with talc [16,17,31], and it is possible that surface characteristics associated with mineralogical variability may also affect the carcinogenic potential of mineral fiber. Since 1981, many reviews of both animal and human data relating to asbestos exposure have been written and little has changed with respect to the dimensional hypothesis [32-38]: the narrower the amphibole-asbestos is, the more likely it is to produce mesothelioma. Furthermore, and perhaps most importantly, although numerous mining populations have been studied, no association between mesothelioma and the inhalation of amphibole has been demonstrated unless the amphibole is asbestiform [2, 39-43]. Furthermore, when amphibole-asbestos is crushed extensively and the asbestiform habit is wholly or partially destroyed, animal experiments indicate that its carcinogenic potential is reduced or eliminated entirely [25,37].

Amphibole-asbestos is also known to cause lung cancer and asbestosis. There appears to be the same relationship between the potential to produce lung cancer and fiber size that there is for mesothelioma: the potency of airborne fibers to produce lung cancer appears to be lower where

airborne fibers are relatively coarse [2]. Furthermore, there is no compelling evidence that lung cancer and asbestosis can be attributed to the inhalation of amphibole unless that amphibole is asbestiform [2, 38-43].

The question of why the inhalation of amphibole-asbestos can result in lung cancer and mesothelioma has never fully been answered [44,45]. The possibility that the surface chemistry of asbestos is important remains and, in fact, is supported by the results of numerous studies [reviewed in 44-47]. Nonetheless, most attention has been focused on the properties of asbestos and other mineral particles that can be most easily measured, i.e., their dimensions. As analysts, we too focus on morphology since it is morphology that defines the asbestiform habit. However, it is important to remember that there may be many properties that accompany the asbestiform habit that we do not measure. Therefore, we must be sure that when we analyze for asbestos, we apply morphological criteria that are specific for asbestos.

The Definition of Asbestos Fiber

For air-monitoring purposes in occupational settings, the Occupational Safety and Health Administration defined an asbestos fiber as any particle of asbestos longer than 5 μm with an aspect ratio of 3 or greater [48]. This morphological standard originated in England as the result of an air-monitoring program in an asbestos textile factory. The 5 μm length was chosen as a lower limit because the optical microscope was the instrument being used for monitoring, and studies by Addingley [49] and Lynch et al. [50] had shown that counting of particles less than 5 μm in length leads to imprecise results. The choice of an aspect ratio of 3 was arbitrary [51]. The dimensional definition became fully entrenched in the United States 1973, when, in the Reserve Mine Case, the US District Court accepted as a definition of a fiber any mineral particle that is at least 3 times longer that it is wide [52].

Today, the simplistic "longer than 5, greater than 3:1" cannot be applied as a definition for an asbestos fiber. OSHA's Final Rule dealing with actinolite, tremolite and anthophyllite is quite clear on this subject. In removing the nonasbestiform amphiboles from the asbestos standard, OSHA effectively removed the old definition of a fiber:

> "OSHA does not believe that the current record provides an evidentiary basis to determine "the appropriate aspect ratio and length" for determining pathogenicity. Even if dimensional cut-

> offs were known for asbestos fibers, additional data do not support a standard for all ATA (i.e., actinolite, tremolite and anthophyllite) minerals based on fiber dimension alone" [2].

Since most habits of amphibole cleave into fragments that when longer than 5 μm are also elongated, a 3:1 aspect ratio is not specific for the asbestiform habit. While OSHA believes that fiber dimension is the most significant indicator of fiber pathology, they state "..the evidence which is available more likely associates fibers with dimension common to asbestos populations with disease causing potential" [2]. By this statement, OSHA effectively directs us as analysts to look for *populations* of fibers with dimensions of asbestos, and only the asbestiform habit will produce a population of particles with the appropriate dimensions. Therefore, we are really analyzing for the *habit* of amphibole-asbestos, not for a particular particle size and shape.

It may be possible to continue to use the criteria of longer than 5 μm and 3:1 or greater aspect ratio for counting airborne particles in an atmosphere known to contain asbestos, such as during or after an abatement procedure. However, the analyst must be sure that it is only asbestos that meets these criteria. If other elongated minerals are airborne, the analysis will be in error.

The Analysis of Bulk Samples

When an analyst receives a sample and is asked to determine if asbestos is present, and if so, how much, he/she must apply a set of criteria to answer this question, and these criteria must be applied to populations of particles, not to particles individually. The first question to be answered is "Is there an asbestiform mineral in the sample?". In other words, is there a population of fibers longer than 5 μm that displays the following characteristics:

1) Mean aspect ratios of individual fibers ranging from 20:1 to 100:1,
2) Bundles of fibers often displaying splayed ends,
3) Very thin fibers, mean widths generally less than 0.5 μm, and
4) Curvature in the longest fibers usually common.

These characteristics of asbestos have been documented for amphiboles implicated in human disease [*5,9-11,13, 15-19,22,32,53-55*]. It is important to note that bundles and matted masses sometimes do not have the extremely high aspect ratios characteristic of the fibrils that make them

up. Whether elongated or not, bundles and matted masses of fibers that meet the criteria should be considered asbestiform.

There is often expressed a concern that an analysis that relies on optical microscopy might result in a false negative because the width of asbestos fibrils is below the resolution of the microscope. There are two reasons why this is unlikely to be the case. First, several studies have shown that fibers of amosite and crocidolite are visible by light microscopy, notably phase contrast, if their width is greater than about 0.1 to 0.15 μm [56-58] even though 0.15 μm is below the resolution of the microscope. Resolution and visibility are different: resolution is a mathematical approximation of the minimum distance by which two points can be separated and still be seen as separate. It is a function of the optics of the microscope. Visibility of course depends on size but equally important is the contrast in index of refraction with the surrounding medium [*59*]. The second reason that asbestos is unlikely to go undetected is that those fibers that are truly invisible in general make up only a small portion of the mass of amphibole-asbestos although they are very abundant and, in fact, may make up the majority of the asbestos fiber population. Modeling the distribution of the mass of asbestos fibers allows an estimate of the percentage of mass that might be invisible by optical microscopy [7, *60*]. The worst case is presented by crocidolite from the Cape Province and Australia, material that is characterized by very small fibrils. If crocidolite is well dispersed, as much as 70% of the mass could be 'invisible' (width less than 0.1 μm). However, in most bulk samples, crocidolite is not uniformly dispersed and the fraction of mass that is visible is likely to be much higher than 30%. For other types of amphibole-asbestos, the model predicts that more than 90% of the mass would be visible. In my experience, asbestos as a naturally occurring trace *contaminant* in industrial mineral products is most likely to be tremolite-asbestos, actinolite-asbestos or anthophyllite-asbestos. (Because of the restricted geologic environments in which they occur, crocidolite and amosite are almost never encountered.) Modeling of the dimensional data for these more common varieties suggests that over 98% of the mass should be visible by optical microscopy. Therefore, it is highly likely that amphibole-asbestos would be detected by optical microscopy in a bulk sample if it is present in an amount greater than about 0.1 wt.%.

Once asbestiform fibers have been found, the analyst must determine which mineral they are because amphiboles and serpentine are not the only minerals to crystallize in an asbestiform habit. For example, nemalite is the asbestiform variety of brucite ($MgOH_2$) and agalite and fibrous talc have been used to designate the asbestiform variety of talc.

Other somewhat common minerals that may develop the asbestiform habit include sepiolite, palygorskite, erionite, and tourmaline. Evidence on the carcinogenicity of asbestiform minerals that are not asbestos is mixed, but there is no compelling evidence that all asbestiform minerals are carcinogenic. Different minerals have different biodurability (survival *in vivo*), surface chemistry, friability, especially friability *in vivo*, and bioavailability, differences that influence their biological activity (reviewed in [*61*]. For example, xonotlite, $Ca_6Si_6O_{17}(OH)_2$, commonly found in an asbestiform habit, is soluble in water.

Mineral identification by optical microscopy requires the use of a petrographic (polarizing light) microscope. Normally, the most reliable property for the identification of a mineral by optical microscopy is the magnitude of the indices of refraction. Many misidentifications of minerals that are fibrous and/or asbestiform could have been avoided by carefully measuring indices of refraction. Minerals may show dispersion staining colors of light yellow or light blue when they are in oils that have indices of refraction that are quite different from those of the mineral, especially when the index of refraction is greater than 1.600. These colors do not indicate a "match", a fact that can be easily confirmed by examining the colors and relative intensities of Becke lines. For mineral identification, at least two (preferably principal) indices of refraction (n_D) should be measured with a precision of at least 0.005 or better. If a mineral possesses other characteristic properties, such as the negative elongation and distinctive blue color of crocidolite, it may be acceptable to measure only one principal index of refraction. It is also extremely important to measure indices of refraction at extinction positions and to relate these directions to morphology. Most texts in optical mineralogy provide diagrams that illustrate the relationships between principal vibration directions and morphology. In the case of fiber bundles, the indices of refraction are not necessarily those given in optical mineralogy texts [Verkouteren and Wylie, in preparation]. For example, the fibrillar structure may result in only two indices of refraction when there should be three. In this case, the maximum and minimum indices of refraction may be slightly less and slightly greater than the reference magnitudes of γ and α respectively.

Optical properties other than indices of refraction, such as color, sign of elongation and birefringence, are usually very helpful in identifying minerals. For fibrous minerals, properties that are derived from an analysis of an interference figure (i.e., 2V, orientation of the optic plane, optic sign and dispersion of the optic axes) are generally not useful because interference figures are almost impossible to obtain on particles smaller than several

micrometers. Furthermore, since asbestos fibers wider than 1 μm are composed of bundles of fibrils, any interference figure would arise from the bundle effect, not the mineral structure.

Care must also be taken in the use of extinction angle in the mineral identification process. First, monoclinic amphiboles that are characterized by oblique extinction will exhibit the characteristic extinction angle only when they lie parallel to (010), a somewhat rare condition for both fibrous and nonfibrous amphiboles. Monoclinic amphiboles that lie parallel to (100) will display parallel extinction and (100) parting may be very common in some specimens. Furthermore, bundles of randomly aligned fibers, the hallmark of asbestos, will show parallel extinction in all orientations [*18*].

There are many analytical techniques other than optical microscopy that can be used to identify minerals. For example, qualitative or quantitative energy dispersive x-ray analysis provides information on the chemical composition and x-ray and electron diffraction provide structural information. These techniques can be used if the optical properties are not sufficient for mineral identification. While these methods are more expensive and time-consuming, they are not as expensive and time-consuming as defending an incorrect analysis.

Conclusions

When OSHA "deregulated" nonasbestiform amphiboles in 1992 [*2*], they placed the burden of identifying asbestos and discriminating it from other habits of amphibole on the analytical community. It may have been simple to look only for 3:1 particles, but it was (and still is) an insufficient criterion by which to identify asbestos. Now we must apply a set of criteria to a *population* of particles. It is appropriate to apply these criteria to a population of particles that is defined by a 3:1 aspect ratio and a 5 μm lower limit of length as long as we recognize that this population discriminator does not define asbestos nor does it define hazardous particles. Within this population, we must identify the particles as amphibole (or chrysotile), and we must find compelling evidence for the asbestiform habit; otherwise, the mineral is simply not asbestos.

References

[1] Occupational Safety and Health Administration, 29 CFR 1910.1001 37 Federal Register, June 7, 1972, p. 11318.

[2] Occupational Safety and Health Administration, Occupational Exposure to Asbestos, Tremolite, Anthophyllite and Actinolite: Final Rule, amendment to